Thermochimica Acta, 184 (1991) 25–31
Elsevier Science Publishers B.V., Amsterdam

Thermooxidation and non-isothermal kinetic study of thermally aged nitrile butadiene rubber

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(Received 23 October 1990)

Abstract

The authors present the results of an attempt to evaluate the non-isothermal kinetic parameters for the oxidation accompanied by release of volatile compounds, of non-aged and thermally aged nitrile butadiene rubber. The values of the non-isothermal kinetic parameters exhibit a compensation effect.

INTRODUCTION

The practical use of polymeric materials requires the knowledge of their behaviour under certain conditions (heat, light, nuclear radiation, humidity, etc). In order to acquire such knowledge one has to investigate the accelerated ageing of the materials by following the change in their properties due to thermo-oxidative degradations. From the results of accelerated ageing experiments, it is possible to evaluate the lifetime of the material under the conditions of its practical use [1]. For thermal degradation, the acceleration factor has to be chosen in such a way that the mechanism of the accelerated degradation of the material should be the same as that of its degradation under the conditions of its practical use. Thermal analysis methods (TG, DTG, DTA and DSC) are very useful in the solution of these problems as they permit the determination of the temperature range of thermal stability [2–6], the values of the non-isothermal kinetic parameters of the degradation [7–9] and the changes undergone by the investigated polymeric materials as a consequence of the accelerated ageing [3,10,11].

This paper deals with our results concerning the thermal behaviour of nitrile butadiene rubber (NBR) submitted to accelerated thermal ageing,

0040-6031/91/$03.50

from derivatographic data. The thermogravimetric curves for both non-aged and thermally aged samples were used to evaluate the non-isothermal kinetic parameters of the thermo-oxidative degradation processes.

EXPERIMENTAL

Nitrile butadiene rubber (NBR) from CATC, Jilava was used.

The heating curves of powdered samples were recorded on a Q-1500 D MOM Budapest-type, Paulik–Paulik–Erdey derivatograph in static air atmosphere, in the temperature range 20–500 ° C at a heating rate of 2.8 K $\min^{-1}$.

The accelerated thermal ageing of the test specimens took place in a WSU-200 oven with forced air circulation in which the temperature was kept constant to ± 2 ° C.

METHODS OF WORKING THE EXPERIMENTAL DATA

Three methods were used to evaluate the non-isothermal kinetic parameters: the Coats–Redfern [12], the Coats–Redfern modified by Urbanovici and Segal [13] and the Flynn–Wall for constant heating rate [14]. The experimental data programs were processed automatically in BASIC [15,16] using a TIM-S computer.

RESULTS AND DISCUSSION

Derivatograms were recorded for non-aged NBR (initial sample) and for NBR aged under the following conditions: 80 ° C with ageing times of 235 and 451 hours; 90 ° C with ageing times of 195, 405 and 600 hours; and 105 ° C with ageing times of 92, 195, 310, 500 and 668 hours.

Figures 1 and 2 show the derivatograms of the non-aged sample and the sample aged at 90 ° C for 195 hours respectively. The thermal curves for the other thermally aged samples are similar to those shown in Fig. 2.

Figure 1 shows two changes, α and β, accompanied by weight loss. The exothermic peak I, located at 250 ° C, corresponds to a process which occurs with a slight increase in sample weight. The β change is accompanied by the exothermic peak II located at 300 ° C. It should be noted that the derivatogram of the non-aged sample located in argon does not exhibit peak I, thus showing that this peak is due to the oxidation of NBR with solid reaction products.

On the derivatograms corresponding to the thermally aged samples, for all the ageing conditions, the DTA curves exhibit two peaks (I and II)

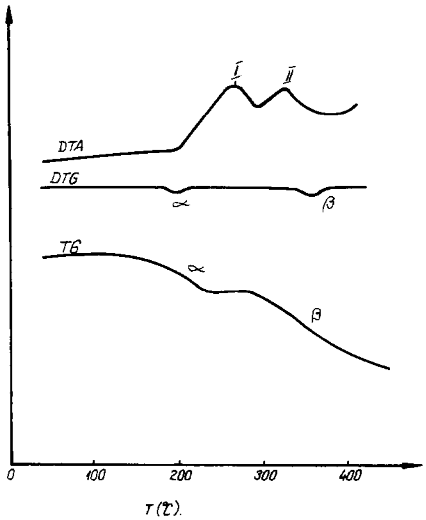

Fig. 1. The derivatogram of non-aged NBR.

located at practically the same temperatures as for the non-aged samples. As with the non-aged samples, peak I is accompanied by a slight increase in weight on the TG curve. The only difference shown by derivatograms of thermally aged samples with respect to that of the non-aged sample is the absence of the α change. This implies that the samples evolve volatile components during thermal ageing.

The non-isothermal kinetic parameters (overall reaction order, n, activation energy, E_A, and pre-exponential factor, A) are listed in Table 1. There

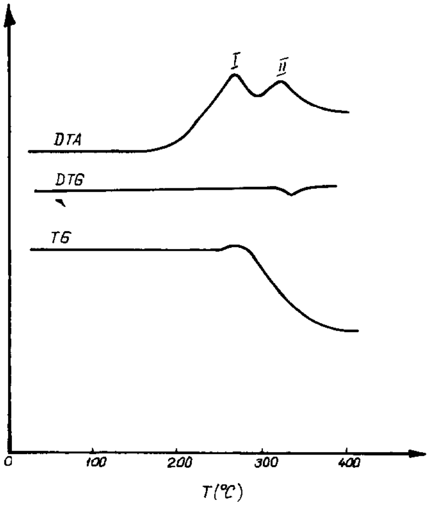

Fig. 2. The derivatogram of NBR aged at 90 °C for 195 h.

TABLE 1

Values of non-isothermal kinetic parameters for the thermo-oxidative degradation of NBR

			Coats–Redfern				Modified Coats–Redfern				Flynn–Wall ($a = ct$)			
No.	T [a] (°C)	t [b] (h)	E_A [c] (kcal mol^{-1})	n [d]	A [e] (s^{-1})	$-r$ [f]	E_A (kcal mol^{-1})	n	A (s^{-1})	$-r$	E_A (kcal mol^{-1})	n	A (s^{-1})	$-r$
1. Initial sample			35.0	2.0	1.44×10^{10}	0.9936	34.9	1.9	1.37×10^{10}	0.9933	35.5	2.0	2.42×10^{10}	0.9944
2.	80	235	44.5	2.4	7.64×10^{13}	0.9907	43.6	2.4	7.53×10^{13}	0.9910	44.7	2.4	6.33×10^{13}	0.9912
3.	80	451	36.7	2.0	4.91×10^{10}	0.9903	36.7	1.9	5.18×10^{10}	0.9899	37.1	2.0	7.64×10^{10}	0.9914
4.	90	195	38.8	1.7	6.96×10^{11}	0.9957	37.8	1.5	2.10×10^{11}	0.9950	39.1	1.7	6.96×10^{11}	0.9957
5.	90	405	39.5	1.9	1.24×10^{12}	0.9960	39.5	1.8	1.32×10^{12}	0.9962	39.7	1.9	1.57×10^{12}	0.9970
6.	90	600	44.2	2.1	7.56×10^{13}	0.9938	44.6	2.0	1.06×10^{12}	0.9920	44.3	2.1	7.86×10^{13}	0.9942
7.	105	92	49.1	2.2	1.24×10^{16}	0.9963	48.2	2.0	5.50×10^{15}	0.9961	48.9	2.2	1.02×10^{16}	0.9966
8.	105	195	48.3	1.8	4.08×10^{15}	0.9970	48.8	1.7	6.70×10^{15}	0.9970	48.1	1.8	3.51×10^{15}	0.9971
9.	105	310	41.7	1.9	8.70×10^{12}	0.9960	42.0	1.8	1.11×10^{13}	0.9960	41.9	1.9	1.02×10^{13}	0.9970
10.	105	500	40.3	1.8	1.99×10^{12}	0.9927	40.4	1.7	2.27×10^{12}	0.9920	40.5	1.8	2.52×10^{12}	0.9934
11.	105	668	58.0	2.6	2.70×10^{19}	0.9906	57.4	2.4	1.57×10^{19}	0.9897	57.3	2.6	1.62×10^{19}	0.9913

[a] T, temperature of thermal ageing.

[b] t, time of thermal ageing.

[c] E_A, activation energy.

[d] n, apparent reaction order.

[e] A, pre-exponential factor.

[f] r, correlation coefficient of the linear regression.

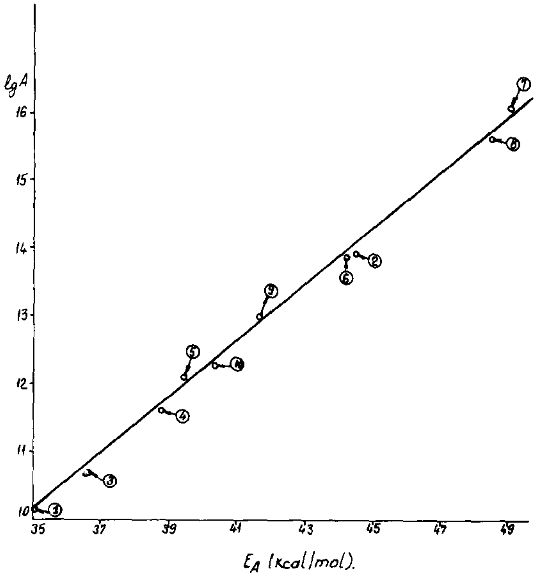

Fig. 3. The plot of log A versus E_A for the thermo-oxidative degradation of NBR. The numbering of the experimental points corresponds to the numbering of the samples in Table 1.

is quite good agreement among the values of the non-isothermal kinetic parameters obtained by the different applied methods. The values of the reaction order for the non-aged and aged samples fall around 2 (with relatively higher deviations from this value due to experimental errors for samples 2, 4 and 11 (see Table 1)). Thus, the thermo-oxidation with evolution of volatile products occurs according to the same mechanism.

The results listed in Table 1 show that the values of E_A and A depend on the conditions of the thermally accelerated ageing. Nevertheless, as shown in Fig. 3, these values can be correlated by the relationship

$$\log A = aE_A + b \qquad (1)$$

where $a = 0.4114$ mol kcal^{-1} and $b = -4.2613$, with $r = -0.99832$ where r is the correlation coefficient of the linear regression. Relationship (1) corresponds to the well known “compensation effect”, observed in many heterogeneous solid–gas chemical reactions [17–19].

According to Agrawal [18], the existence of a compensation effect requires, in addition to a linear relationship of the form of eqn. (1), an intersection of the Arrhenius plots. The temperature corresponding to this intersection is known as the isokinetic temperature (T_i). Figure 4 shows the extent to which Agrawal’s criterion is satisfied. The separate position of straight line 2 is probably due to the relatively high deviation of its reaction order, $n = 2.4$, compared with the reaction orders of the other samples which fall around $n = 2$. Actually, as seen from Fig. 4, the Arrhenius plots

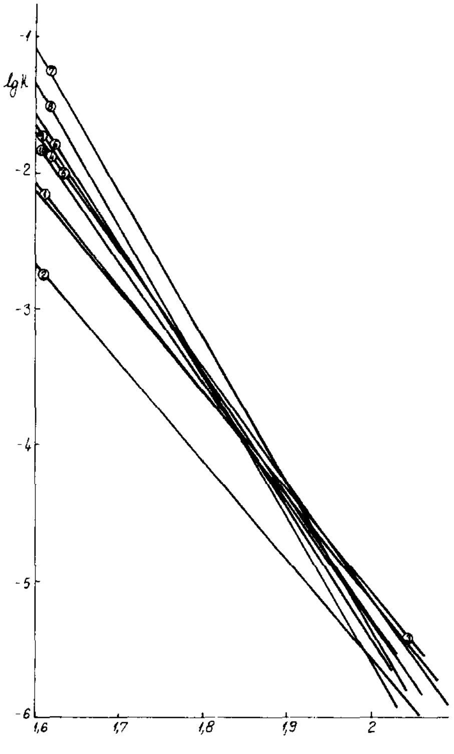

Fig. 4. Arrhenius plots for the thermo-oxidative degradation of NBR. The numbering of the Arrhenius plots corresponds to the numbering of the samples in Table 1.

do not intersect at a point but in a range corresponding to "isokinetic" temperatures between 250 and 290 °C, probably due to the inherent errors in the evaluation of rate constants from non-isothermal data. In fact, Zsakó and Somasekharan [20] have shown that only for $r = 1$ on the plot of log A, against E_A do the Arrhenius straight lines intersect at a single point.

The isokinetic temperature was calculated from the slope of the straight line of log A against E_A using the relationship [17–19]

$$T_i = \frac{1}{2.303Ra} \qquad (2)$$

The value determined, $T_i = 258$ °C, lies within the previously mentioned range of isokinetic temperatures.

CONCLUSIONS

The non-isothermal kinetic parameters of the thermo-oxidative degradation of non-aged and thermally aged samples of NBR have been evaluated using three methods which yield values which are in satisfactory agreement. The values of log A and E_A show the presence of compensation effect.

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